
TECHNICAL REPORT R-108

MEASUREMENTS OF THE DISSOCIATION RATE OF MOLECULAR OXYGEN

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**Langley Research Center
Langley Field, Va.**

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SUMMARY

The ability of molecular oxygen to absorb light in the Schumann-Runge ultraviolet region of the spectrum has been used to follow the change in concentration of molecular oxygen as a function of time behind shock waves in oxygen and in a mixture of 10-percent oxygen in argon.

Analysis of the records obtained yielded values for the dissociation rate of oxygen as a function of temperature over the range $4,000^{\circ}$ to $10,000^{\circ}$ K. The highest previously reported experimental results in the literature were at $7,500^{\circ}$ K. The results are expressed in the form of straight-line Arrhenius plots which were fitted to the data by using a least-squares criterion. Agreement of the magnitude of the measured dissociation rates with experimental rates from the literature is satisfactory, but the observed temperature dependence is considerably weaker than that predicted by the usual theoretical treatments.

INTRODUCTION

The dissociation rate of molecular oxygen is an important parameter in the study of the flow of high-temperature air. Many theoretical estimates of this rate have appeared in the literature. Most of these, such as in references 1 to 4, were introduced only incidentally, because they were needed for the work at hand, but a few papers, such as references 5 to 7, have appeared which were chiefly concerned with the theoretical evaluation of this rate. It is evident from treatments of the general theory of reaction rates (for example, ref. 8) that theoretically derived rates are useful as a guide but that experimental determinations must be made ultimately.

This report is concerned with experimental measurements of the O_2 dissociation rate behind

strong shock waves in oxygen and in a mixture of 10-percent oxygen in argon. The changing concentration of oxygen molecules at a given point in a shock tube was determined by using an ultraviolet absorption method developed independently by the National Aeronautics and Space Administration (refs. 9 and 10) and by Avco-Everett Research Laboratory (refs. 11 to 13). The strong continuum absorption of O_2 in the spectral range 1,300 to 1,750 angstrom units was used to measure O_2 concentration as a function of time and the temperature and density of the hot gas sample were calculated from the measured speed of the shock wave.

Experimentally measured oxygen dissociation rates have also been reported in the literature. Reference 13 used the ultraviolet absorption method. References 14 and 15 based their results on interferometric measurement of the change in gas density produced by dissociation. Reference 16 followed the change in gas density but used the absorption of soft X-rays in xenon (which was added as a tracer gas) instead of an interferometer. Reference 17 used the detachment distance of the bow shock wave on spheres moving at high velocity through oxygen.

The ultraviolet absorption method is to a certain extent a more satisfying approach than the others because the records obtained depend directly on the concentration of oxygen molecules present in the test sample. It should be pointed out, however, that the O_2 concentration is a function of gas density as well as of the degree of dissociation and that the amount of light absorbed by a given concentration is determined by the temperature-dependent absorption coefficient. A simultaneous use of the ultraviolet absorption method with either the interferometric or the

X-ray absorption method appears to be desirable. However, these methods have not been combined.

SYMBOLS

A	pre-exponential term in the Arrhenius equation
D_0	dissociation energy, cal/mole
D_{eff}	effective dissociation energy, cal/mole
d	distance particle travels to reach observation point, cm
d'	distance of shock wave from observation point, cm
f_1, f_2	functions
g	mole-fraction of oxygen in gas mixture before dissociation (oxygen, $g=1.000$; oxygen-argon, $g=0.1007$)
J	intensity of transmitted light, erg/cm ² -sec
J_0	intensity of incident light, erg/cm ² -sec
K_c	equilibrium constant based on concentration, molecules/cm ³
K_p	equilibrium constant based on partial pressures, atm
k_d	dissociation rate constant, cm ³ /molecule-sec
k_r	recombination rate constant, cm ⁶ /molecule ² -sec
l	absorption-path length, cm
M_1	shock Mach number
N	Avogadro's number, 6.025×10^{23} molecules/mole
p	pressure, atm or mm Hg
R	universal gas constant, 82.05 cm ³ -atm/mole-°Kelvin or 1.987 cal/mole-°Kelvin
T	temperature, °Kelvin
t	particle time, microsecond
t'	laboratory time, microsecond
v	particle velocity, cm/sec
v'	velocity of shock wave, cm/sec
X	total number of molecules and atoms present in testing medium
α	degree of dissociation
ϵ	absorption coefficient, cm ⁻¹

$$A = \left(\frac{N p_1}{R T_1} \right) \sigma (g - \alpha) (1 + \alpha) - \left(\frac{N p_1}{R T_1} \right)^2 \sigma^2 \left(\frac{4 R T_2}{N K_p} \right) \alpha^2 (1 + \alpha), \text{ molecules/cm}^3 \text{ (eq. (11))}$$

μ_1	molecular weight of undissociated gas, g/mole
ρ	gas density, g/cm ³
$\hat{\rho}$	reduced gas density, $(g - \alpha)(\rho/\rho_s)$

σ	density ratio, ρ_2/ρ_1
τ_D	dissociation relaxation half time, microsecond
τ_V	vibration relaxation half time, microsecond
$[]$	concentration, molecules/cm ³
Subscripts:	
1	conditions in front of shock wave
2	conditions behind the shock wave
s	standard conditions for temperature and pressure

EXPERIMENTAL DETERMINATION OF DISSOCIATION RATE

DESCRIPTION OF EXPERIMENTAL WORK

The light sources, monochromator, shock tube, and other related equipment used in this investigation have been described in detail in references 10 and 18; only a short description is given here. Figure 1 shows a schematic diagram of the experimental equipment.

The dissociation-rate measurements were made in a double diaphragm shock tube with either oxygen or a mixture of 10-percent oxygen in argon as the test gas. Bursting the main diaphragm with either high-pressure hydrogen or helium produced a shock wave that compressed and heated the buffer gas, helium, in the second chamber. This high-temperature and high-pressure buffer gas burst a smaller second diaphragm to produce a shock wave in the 1-inch channel where the test gas was located.

Commercial-grade oxygen and argon were used in all of the tests. The oxygen content of the 10-percent mixture was determined by using a standard pyrogallol procedure like that described

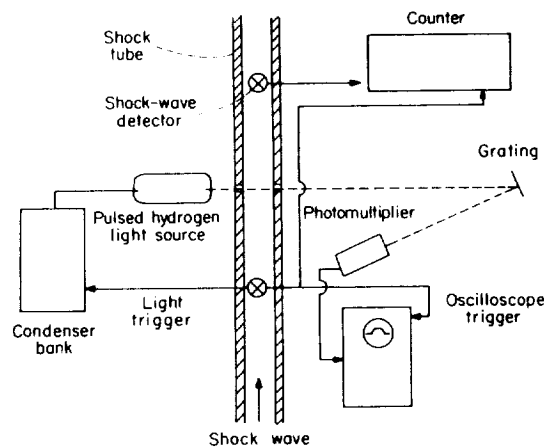


FIGURE 1. Schematic diagram of equipment.

in reference 19. This was done before any test runs were made and was repeated after all the runs had been completed. The result was 10.07 ± 0.10 percent oxygen. The test gas was passed through a drying agent at high pressure before every run to remove any water vapor present. A continuous purging system was used to insure the purity of the gas against any air leaks in the channel of the shock tube.

The pressure of the gas in the channel was measured with an Alphatron vacuum gage and two dial gages. All the gages were calibrated by using a McLeod gage as the standard. The initial temperature of the test gas was measured before each run by the use of a mercury-in-glass thermometer mounted near the shock tube.

The test section was located 14 feet from the second diaphragm to insure complete formation of the shock wave and 3 feet from the end of the shock tube to prevent any shock reflections from interfering with the tests. Two removable window holders with thin disks of lithium fluoride cemented to the ends were used as test-section windows. The slit openings were 1 millimeter wide and 3 millimeters high, positioned so that the light beam traversed the shock tube at right angles to the flow. The optical path length in the test section was 1.0 inch.

Ion-gap-type velocity stations located 5 inches in front of and 5 inches behind the test section were used to determine the velocity of the shock wave in the test section. Signals from the ion-gap detectors triggered type 2D21 thyristors. The pulses from these were fed to a Berkeley counter to measure the transit time of the shock wave between the two stations and were also used to trigger the light source and the oscilloscope sweep.

The ultraviolet light used in the experiment was obtained by discharging a bank of coils and condensers arranged to provide a pulse of light for a duration of 100 microseconds. The discharge took place in a narrow-bore quartz tube containing flowing hydrogen gas. Light from the source passed through the test section perpendicular to the flow in the shock tube. The grating monochromator permitted only a narrow range (± 11 angstrom units) of the ultraviolet spectrum to fall on a DuMont Type 6292 photomultiplier tube which had been sensitized for ultraviolet light by coating it with sodium salicylate. The optical

path from the exit window in the shock tube to the photomultiplier tube was kept evacuated to prevent any unnecessary absorption of ultraviolet light. The output from the photomultiplier tube was fed to a Tektronix type 545 oscilloscope and was recorded by a Polaroid Land camera. The rise time of the electronics was of the order of $\frac{1}{2}$ microsecond.

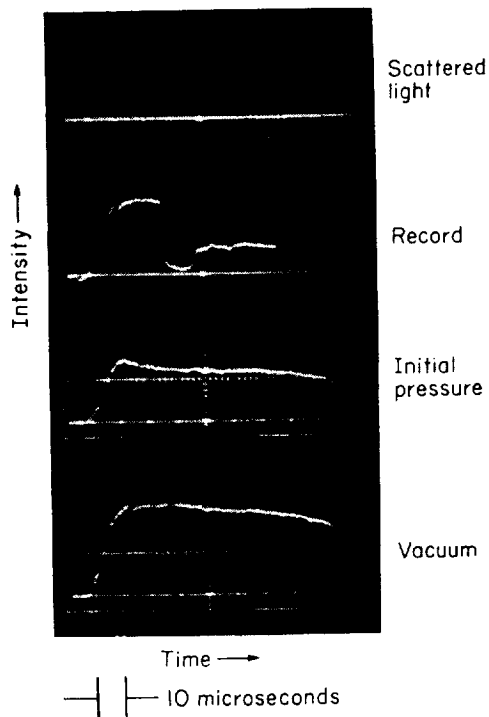
Figure 2 shows four typical records obtained. The traces marked "Vacuum" show the intensity of the light obtained with approximately 1 micron of pressure in the shock tube; the traces marked "Initial pressure" show the intensity obtained with the test gas at a pressure p_1 ; and the traces marked "Record" were obtained for the runs. The values of p_1 for the oxygen tests were usually on the order of 0.5 mm Hg, whereas for the oxygen-in-argon tests the initial pressures were on the order of 4.0 mm Hg. On some of the photographs a "Scattered light" trace was obtained. Because the oxygen present in air at atmospheric pressure absorbs ultraviolet light completely in the range of the test wavelengths used, the monochromator was opened to the atmosphere so that the amount of scattered light getting through the monochromator could be determined.

DATA ANALYSIS

Figure 3 is a drawing which represents a typical oscilloscope record for a test in oxygen. The line at the bottom of the diagram shows a single sweep with the ultraviolet lamp turned off and corresponds to complete absorption of the beam with the lamp on. The broken line is the trace that would appear if no absorption occurred in the test section. The solid line is the trace at pressure p_1 that is triggered by the shock wave as it approaches the test section. The discontinuity in this trace indicates the arrival of the shock wave in the test section and is chiefly due to the sudden increase in the gas density across the shock front. After this jump, there is a gradual change which is due to a combination of three effects:

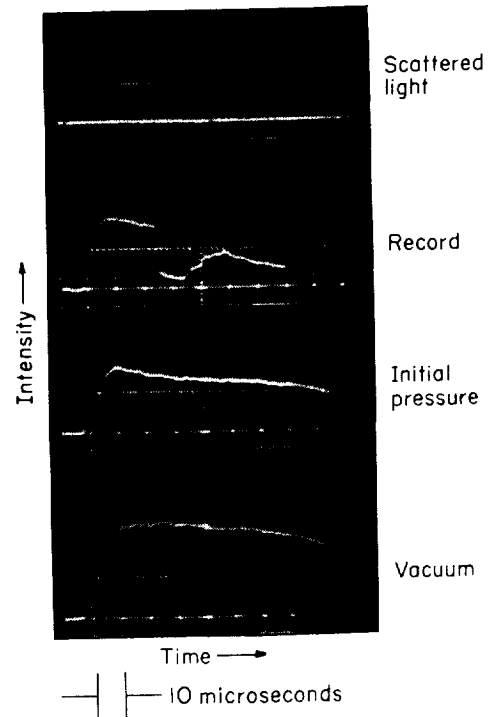
- (1) Because of dissociation, the concentration of oxygen molecules is decreasing
- (2) The lowering of the equilibrium vibrational temperature which accompanies the dissociation affects the value of the absorption coefficient of molecular oxygen
- (3) The gas density increases as dissociation proceeds.

$T_1 = 296.0^\circ \text{K}$; $p_1 = 0.768 \text{ mm Hg}$;
 $M_1 = 10.33$; $T_2 = 4,983^\circ \text{K}$

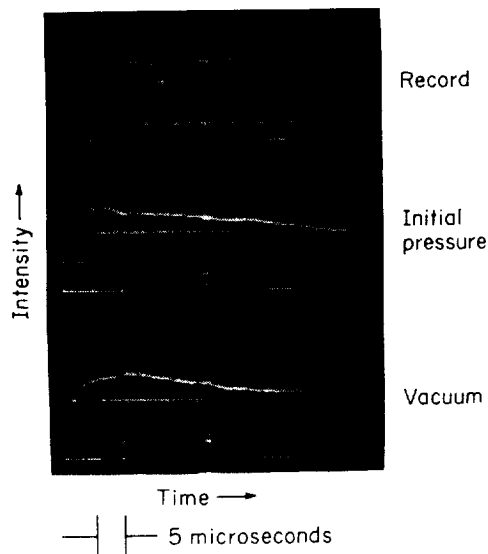


Oxygen

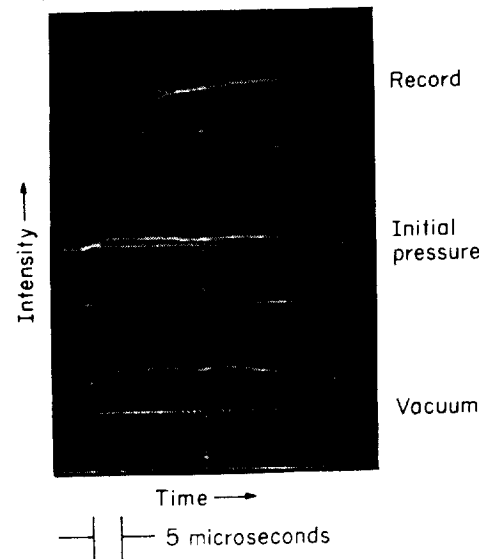
$T_1 = 296.5^\circ \text{K}$; $p_1 = 0.635 \text{ mm Hg}$;
 $M_1 = 9.68$; $T_2 = 4,477^\circ \text{K}$



$T_1 = 299.0^\circ \text{K}$; $p_1 = 3.205 \text{ mm Hg}$;
 $M_1 = 9.11$; $T_2 = 7,276^\circ \text{K}$



$T_1 = 298.0^\circ \text{K}$; $p_1 = 4.955 \text{ mm Hg}$;
 $M_1 = 8.35$; $T_2 = 6,159^\circ \text{K}$



10-percent oxygen in argon

FIGURE 2.--Typical shock-tube records. The wavelength used was 1,550 angstrom units.

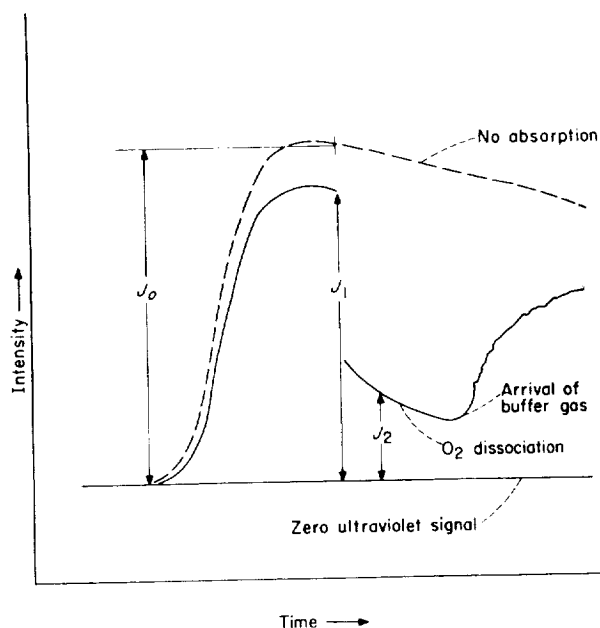


FIGURE 3. Diagram illustrating measurements made on records.

The rise in the transmitted intensity toward the end of the record indicates the arrival of the buffer gas and thus the end of the observation of the effect of dissociation. The time between the passage of the shock front and the contact surface was observed to be considerably shorter than that established by simple shock-tube theory. Reference 20 shows that this is an effect to be expected in small-diameter shock tubes operated at low initial pressures. This reference also indicates that the temperature and density of the flow in the region between the shock front and contact surface may also deviate from that predicted by simple shock-tube theory. No corrections were applied for this in calculating the density ratio and temperature behind the shock front. The use of the oxygen-in-argon mixture allowed tests to be run at higher initial pressures so that longer testing times could be obtained.

The equation $\frac{J_1}{J_0} = e^{-\epsilon_1 \hat{\rho}_1 l}$ represents the light intensity ratio before the shock wave passed the test section and the equation $\frac{J_2}{J_0} = e^{-\epsilon_2 \hat{\rho}_2 l}$ represents the light intensity ratio after the passage of the shock wave. The quantity $\hat{\rho} = (g - \alpha)\rho/\rho_s$ is called the reduced gas density and is introduced for convenience. Note that $\hat{\rho}_1 = g \frac{\rho_1}{\rho_s}$ and that

$\hat{\rho}_2 = (g - \alpha) \frac{\rho_2}{\rho_s} = \left(\frac{g - \alpha}{g} \right) \sigma \hat{\rho}_1$ where $\sigma = \frac{\rho_2}{\rho_1}$ and ρ_2 varies with distance behind the shock front. Since the intensity of the light flashes was not reproducible, the two intensity ratio equations were combined into the following equation, which does not include J_0 .

$$-\log_e \frac{J_2}{J_1} = \hat{\rho}_1 l \left(\frac{g - \alpha}{g} \sigma \epsilon_2 - \epsilon_1 \right) \quad (1)$$

According to reference 2, the state of a gas which is dissociating behind a shock wave can be calculated as a function of the degree of dissociation α even though the rate of dissociation is unknown. Then experimental measurements of the gas properties as functions of time behind the shock front can be matched to the calculated properties to determine the unknown rate constant. This procedure was followed. The density ratio σ and the absorption coefficient ϵ were calculated as functions of the degree of dissociation α and were used in equation (1) to determine theoretical J_2/J_1 ratios as functions of α . Experimentally determined ratios of J_2/J_1 as functions of time were then used to establish the relation between degree of dissociation and time which is necessary for the rate analysis.

For this analysis molecular oxygen was assumed to be the only component which absorbed the ultraviolet wavelengths used. Values of ϵ as a function of temperature for various wavelengths were taken from reference 10. The best-estimate values listed there were used and it was assumed that all the electronic states of O_2 were excited behind the shock waves in oxygen, and that only the ground electronic state of O_2 was excited behind shock waves in the mixture of oxygen in argon. The possible existence of weak absorption of ultraviolet light by high-temperature argon which was pointed out in reference 10 was found to have a negligible effect on the rate analysis.

To obtain the σ and T values needed in the analysis, a graphical solution was made by using the equation of state and the conservation equations as outlined in reference 2. The results are shown in figures 4 and 5 as functions of shock Mach number M_1 and degree of dissociation α . Vibrational equilibrium was assumed for all these results and no records were analyzed for which vibration was not believed to be in equilibrium. (See ref. 10 in which the same records were used to study the temperature dependence of ϵ .)

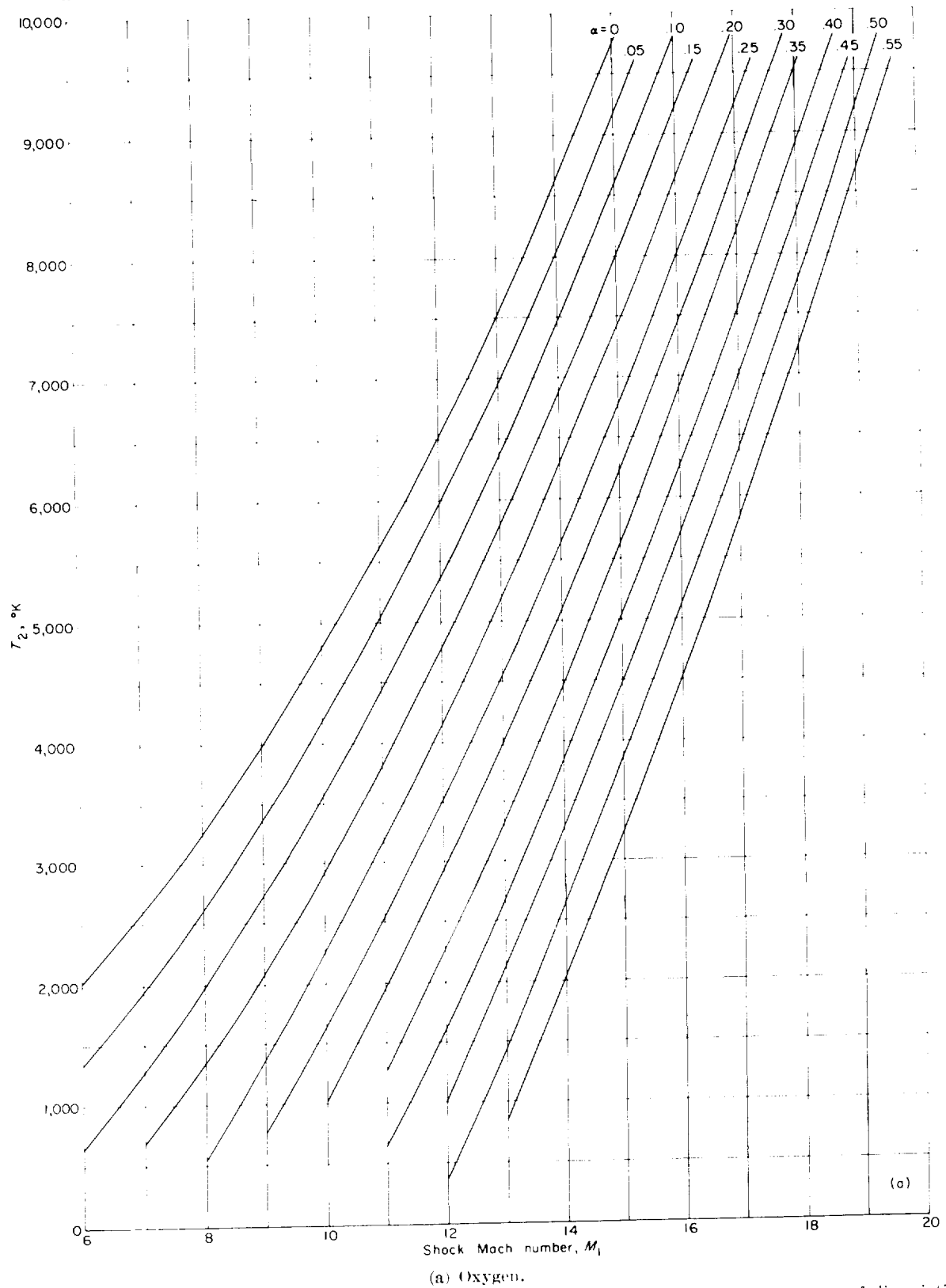
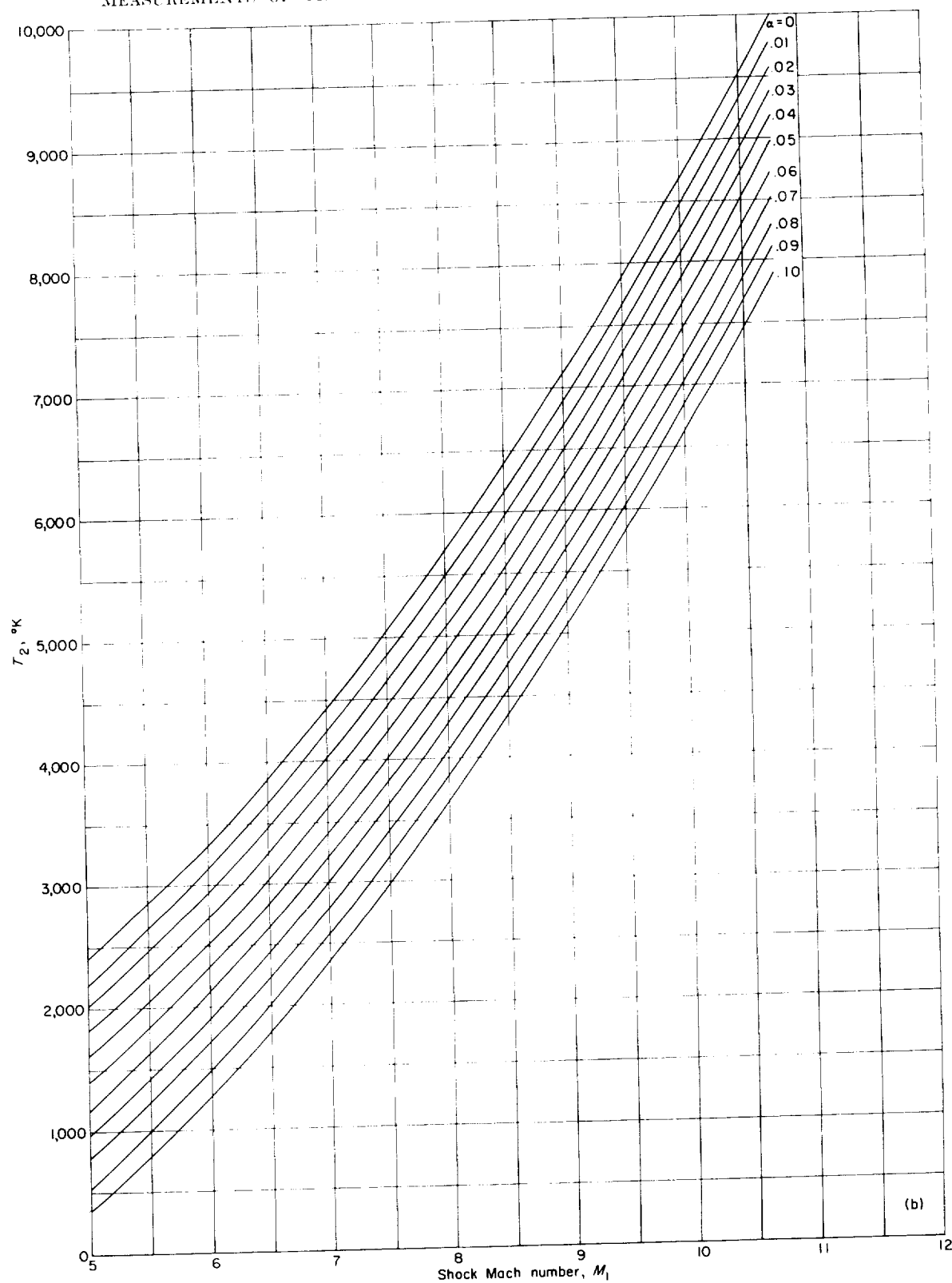


FIGURE 4: Calculated values of temperature as a function of shock Mach number for various degrees of dissociation. $T_1 = 300^\circ K$.



(b) 10-percent O_2 in Ar.
FIGURE 4. - Concluded.

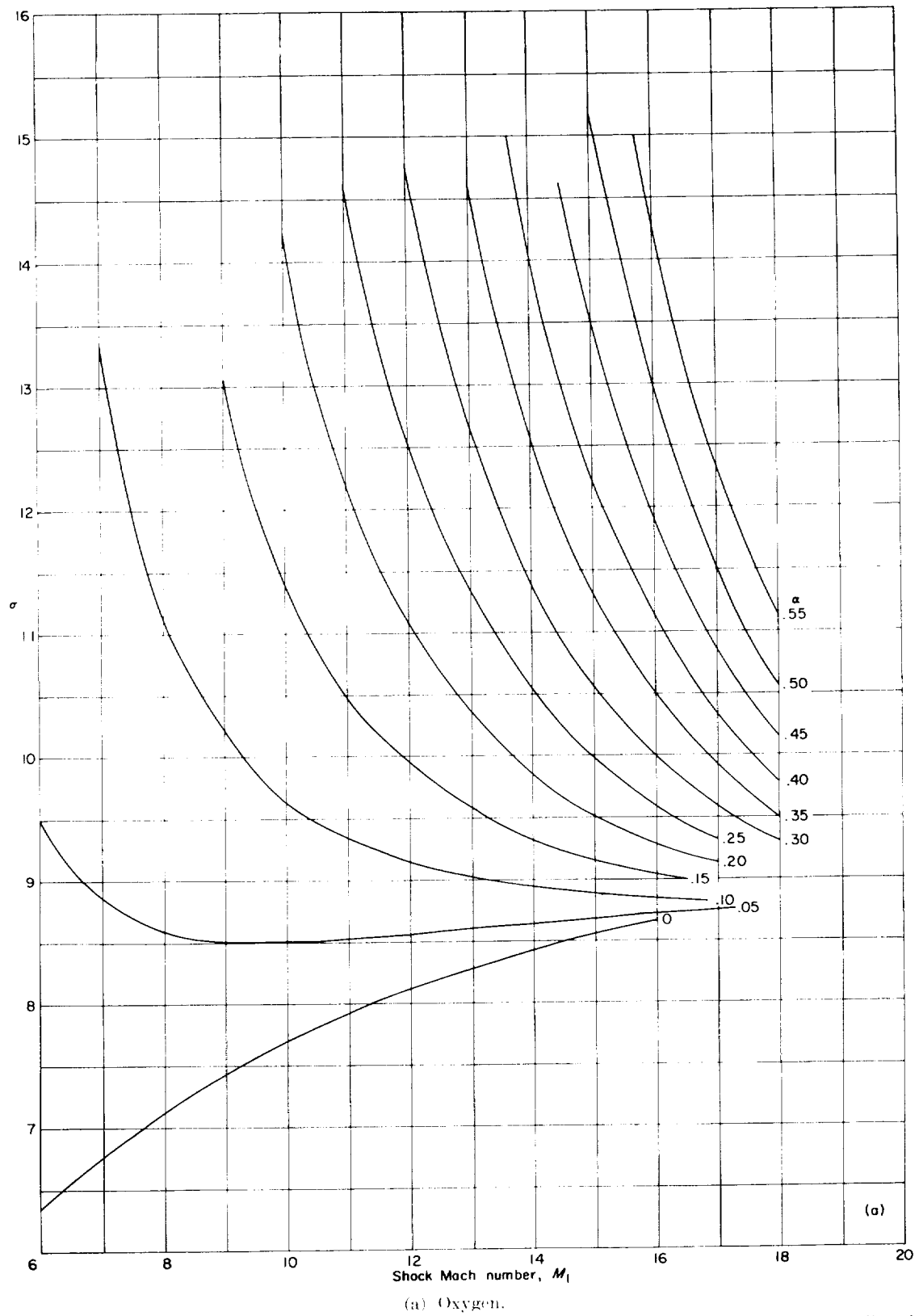
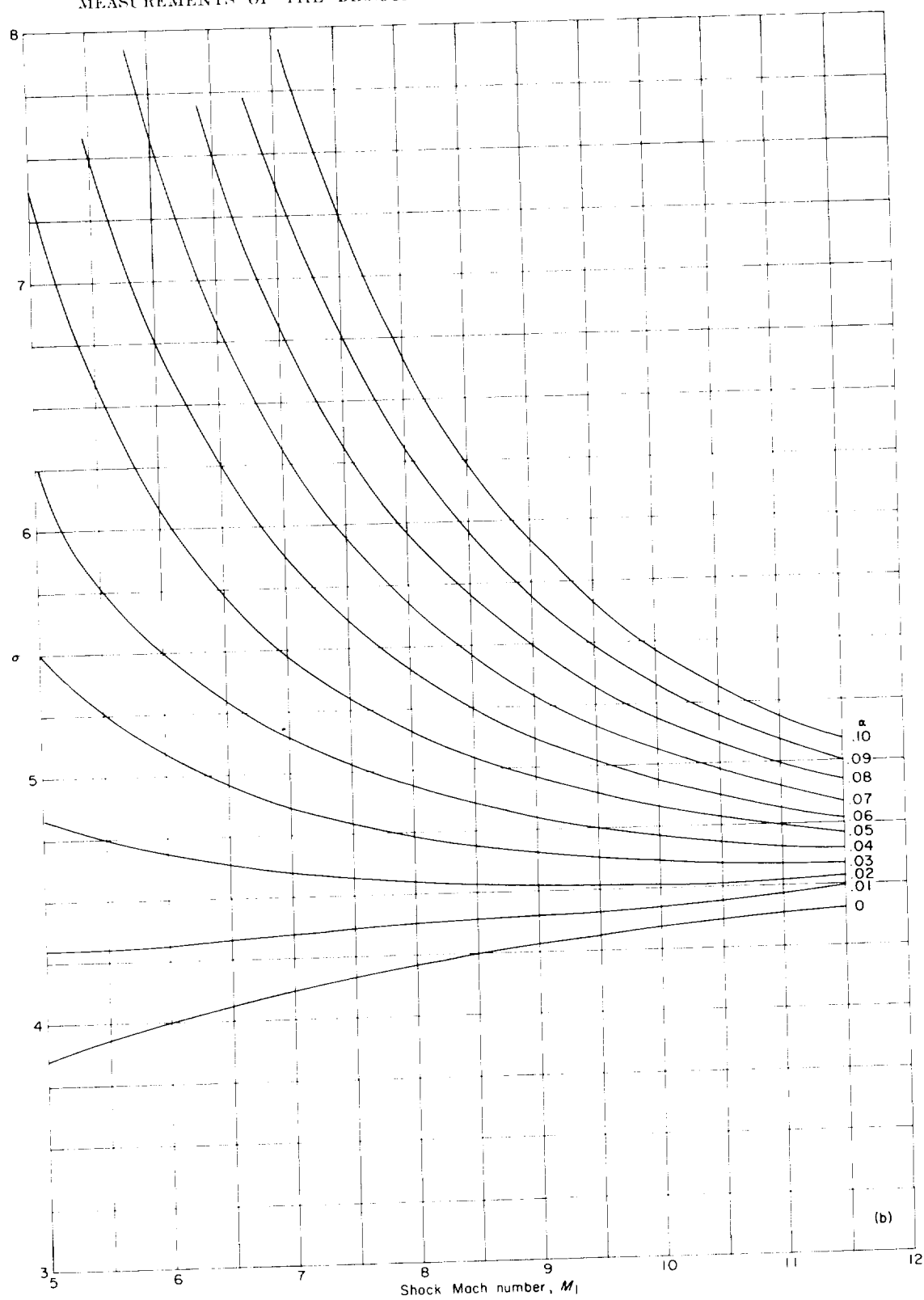


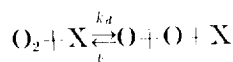
FIGURE 5. Calculated values of density ratios as a function of shock Mach number for various degrees of dissociation.



(b) 10-percent O_2 in Ar.
FIGURE 5. Concluded.

The effect of ionization was neglected in calculating the density ratio and temperature behind the shock front since reference 21 shows that ionization is negligible in O_2 below $M_1=20$ and reference 22 estimates that ionization relaxation times in argon for pressures on the order of 5 mm Hg are greater than 100 microseconds for temperatures less than $10,000^\circ K$.

The dissociation process for molecular oxygen was assumed to be the result of bimolecular collisions as follows:



where X can be any type of atom or molecule present. All types of collision partners were assumed to be equally efficient. Any differences in efficiency were expected to show up in the comparison of the rates measured in pure oxygen to those measured in the oxygen-in-argon mixture.

The concentrations of the various components of the gas mixtures present in any of the shock-tube tests can be expressed as follows:

$$[O_2] = (g - \alpha) \left(\frac{N}{\mu_1} \right) \rho_2 = (g - \alpha) \frac{\sigma N p_1}{RT_1} \quad (2)$$

$$[O] = (2\alpha) \left(\frac{N}{\mu_1} \right) \rho_2 = (2\alpha) \frac{\sigma N p_1}{RT_1} \quad (3)$$

$$[Ar] = (1 - g) \left(\frac{N}{\mu_1} \right) \rho_2 = (1 - g) \frac{\sigma N p_1}{RT_1} \quad (4)$$

$$[X] = (1 + \alpha) \left(\frac{N}{\mu_1} \right) \rho_2 = (1 + \alpha) \frac{\sigma N p_1}{RT_1} \quad (5)$$

Differentiation of equation (2) gives

$$\frac{d[O_2]}{dt} = \left(\frac{N}{\mu_1} \right) \left\{ (g - \alpha) \frac{d\rho_2}{dt} - \rho_2 \frac{d\alpha}{dt} \right\} \quad (6)$$

The customary equation for bimolecular dissociation and three-body recombination at constant volume is

$$\left\{ -\frac{d[O_2]}{dt} \right\}_{\frac{d\rho_2}{dt}=0} = k_d [O_2][X] - k_r [O]^2 [X] \quad (7)$$

By using equation (6), the left-hand side of this equation can be written as

$$\left\{ -\frac{d[O_2]}{dt} \right\}_{\frac{d\rho_2}{dt}=0} = \left(\frac{N}{\mu_1} \right) \rho_2 \frac{d\alpha}{dt} \quad (8)$$

At equilibrium the following relations hold by definition:

$$K_c = \frac{k_d}{k_r} = \frac{[O]^2}{[O_2]} = \frac{N K_p}{RT} \quad (9)$$

By also assuming that $k_d = K_c k_r$ for nonequilibrium conditions, equations (7), (8), and (9) can be combined and solved for k_d as follows:

$$k_d = \frac{\frac{d\alpha}{dt}}{\Lambda} \quad (10)$$

where

$$\Lambda = \left(\frac{N p_1}{RT_1} \right) \sigma (g - \alpha) (1 + \alpha) - \left(\frac{N p_1}{RT_1} \right)^2 \sigma^2 \left(\frac{4RT_2}{N K_p} \right) \alpha^2 (1 + \alpha) \quad (11)$$

The second term on the right-hand side of equation (11) is due to recombination of atoms to form O_2 and is negligible except near equilibrium. The dissociation-rate constants were derived from the data by using equation (10).

Because the gas behind the shock wave is flowing in the same direction as the shock front, the sample under observation at a given time is continually changing. The particle being observed was heated initially by the shock wave some distance d ahead of the observation point and is traveling at a velocity v . When this particle is at the observation point, the shock wave, which is traveling at a velocity v' , is at a distance d' beyond this point. By assuming constant velocities throughout (that is, no shock attenuation) the observed laboratory time, which is the elapsed time since the shock wave passed the observation window, is given by the relation

$$t' = \frac{d'}{v'}$$

and the particle time, which is the elapsed time since the particle was heated by the passage of the shock wave, is

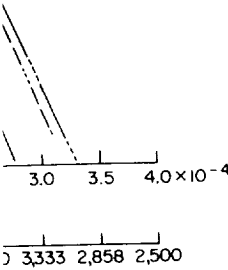
$$t = \frac{d}{v} = \frac{d + d'}{v'}$$

$$d + d' = t' v' + t v = t v'$$

$$t' v' = t (v' - v)$$

$$t = t' \left(\frac{v'}{v' - v} \right)$$

percent O₂ in Ar
percent O₂ in Ar (eq. (14))
percent O₂ in Ar (eq. (15))
(eq. (13))
-and 1-percent O₂ in Ar
(ref. 13)
(ref. 14)
(ref. 17)
percent O₂ in Ar (ref. 15)
-- O₂ (ref. 15)



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The effective disso-
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5), and are as follows:

74.28 kcal/mole
74.66 kcal/mole
102.83 kcal/mole

s are smaller than the
energy of the oxygen

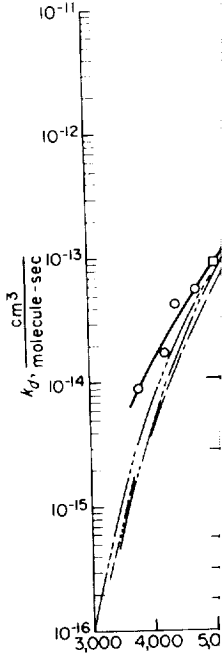


FIGURE 8. The dis-
Literature values, i
lines. All O₂ in
of Ar; for this reas
and (14) and also
cannot be distinguis

molecule *D*₀ = 117.5
simple Arrhenius eq

k_d =

is not an adequa
obtained.

Two values of *D*₀
in-argon mixture k
in the slope in the
tures as shown in
value of *D*_{eff} is th
oxygen-in-argon c
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only the data fr
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which correspond
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much better than
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in figure 7 which
and 15. Althou
did not report a

Since

$$\sigma = \frac{\rho_2}{\rho_1} \left(\frac{r'}{r} \right)$$
$$t = \sigma t'$$
(12a)

If shock attenuation is present, the equation
still holds in the differential form,

$$dt = \sigma dt'$$
(12b)

so that

$$(t)_2 = \int_0^{(t')_2} \sigma dt'$$
(12c)

Equation (10) was used to determine *k_d* in two
different ways:

First, finite increments of *α* and *t* were used to
evaluate *dα/dt* for use in equation (10). This
procedure gave corresponding values of *k_d* and *T*
at Δ*α* = 0.01 intervals for oxygen and at Δ*α* =
0.005 intervals for the oxygen-in-argon mixture.

Second, the quantity *dα/dt* was plotted against
A as shown in figure 6. Isotherms on this plot
should be straight lines which radiate from the
origin and have a slope which is equal to *k_d* at a

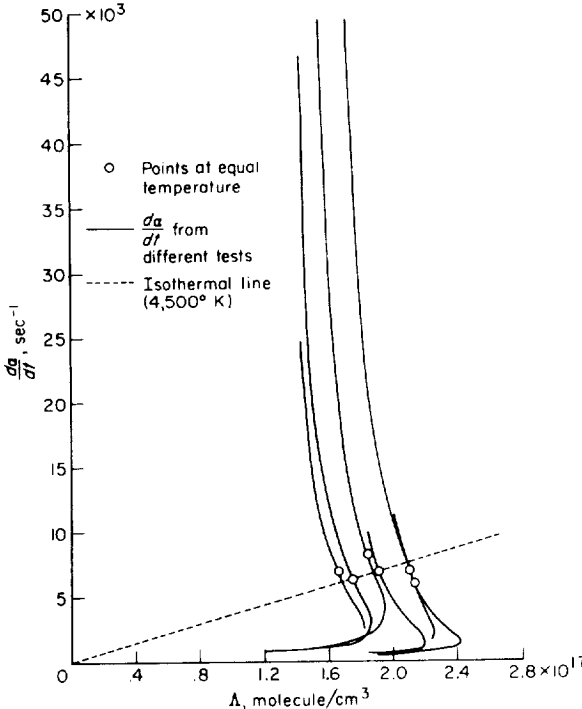


FIGURE 6. Determination of the dissociation-rate con-
stant for oxygen using the isothermal-line method. The
slope of the isothermal line from the origin gives the
value of *k_d* at a given temperature.

particular temperature. In
k_d for a given temperature,
sponding to this temperature
the experimental *dα/dt* plots
from the origin was fitted to

PRESENTATION OF

The experimentally determ
dissociation rate constant *k_d*
I and II and are plotted in
Experimental rate constants
14, 15, and 17 are also shown

The *k_d* values in table I
initial parts of the records.
k_d was determined by what hap
behind the shock front. Thes
I were fitted by straight line
squares criterion of best fit.
as follows:

For the oxygen data (3,800° t

$$\log_{10} k_d = -1.6233 \times 10^4$$

For the oxygen-in-argon data
(K),

$$\log_{10} k_d = -1.6316 \times 10^4$$

Another straight line was
temperature oxygen-in-argon
(7,500° K),

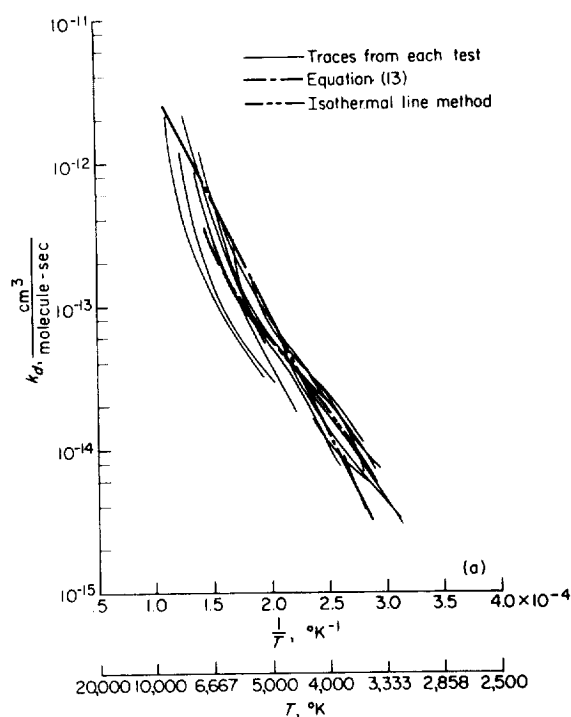
$$\log_{10} k_d = -2.2471 \times 10^4$$

These lines are shown in figur

Figure 9 presents *k_d* value
same photographs as the init
instead of being restricted to
mediately behind the shock w
were determined at many poin
front and produced a trace his
ature variation of *k_d* for each

Table II lists the experimen
from the slopes of isothermal
one that appears in figure 6.

plotted in figure 9 for compar
The experimental rate data
different way in figure 10.
constants *k_d* were derived fr
rate constants *k_d* by using eq



(a) Oxygen.

FIGURE 9.—Experimentally determined values of the dissociation-rate constant. Curves from isothermal-line method, least-square lines, and experimentally determined traces.

they observed, in agreement with the present work, that the k_d values for an oxygen-in-argon mixture above $7,500^\circ\text{K}$ were lower than would be expected from an extrapolation of the data below that temperature. They attributed this to coupling of the dissociation and vibrational relaxation processes at temperatures above $7,500^\circ\text{K}$. No criticism is offered here of the coupling process they proposed. Indeed, it looks very plausible. However, they point out that, once vibration has reached equilibrium, the dissociation process proceeds normally. Thus, if vibration reaches equilibrium in a time interval after the shock passage which is equal to or less than the resolution time of the equipment used, then there is no reason to believe that the analysis of the records obtained would be affected. Figure 11(a) shows that, under the conditions present in the experiments reported here, the laboratory vibrational relaxation times τ_V were equal to or less than the equipment resolution time of approximately 0.33 microsecond for temperatures equal to or greater

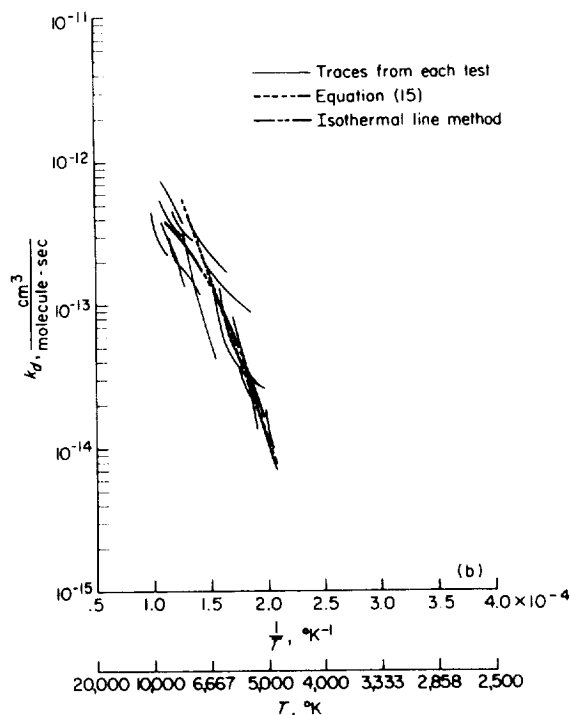
(b) 10-percent O_2 in Ar.

FIGURE 9.—Concluded.

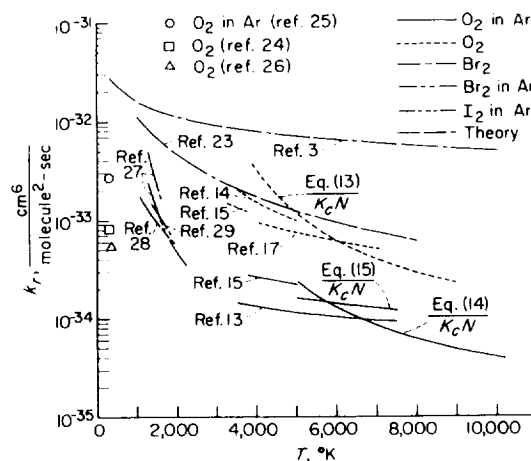
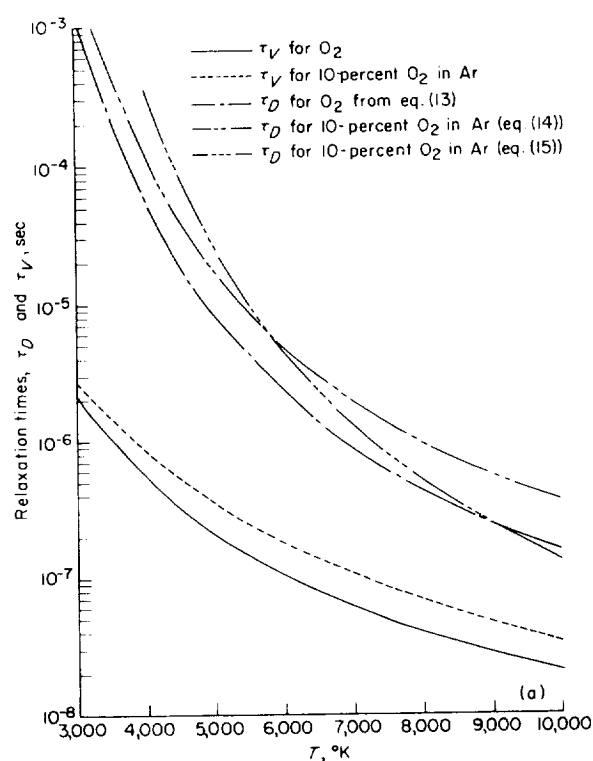


FIGURE 10. Theoretical and experimental recombination-rate constants as a function of temperature. (Where k_d values are given in the literature, the k_r values are calculated by using $k_r = k_d/K_c$.)

than $5,000^\circ\text{K}$. On the other hand, at temperatures less than $5,000^\circ\text{K}$ the dissociation rate is so much slower than the vibration adjustment rate that very little dissociation occurred during the times required to attain vibrational equilibrium. Coupling of vibration and dissociation



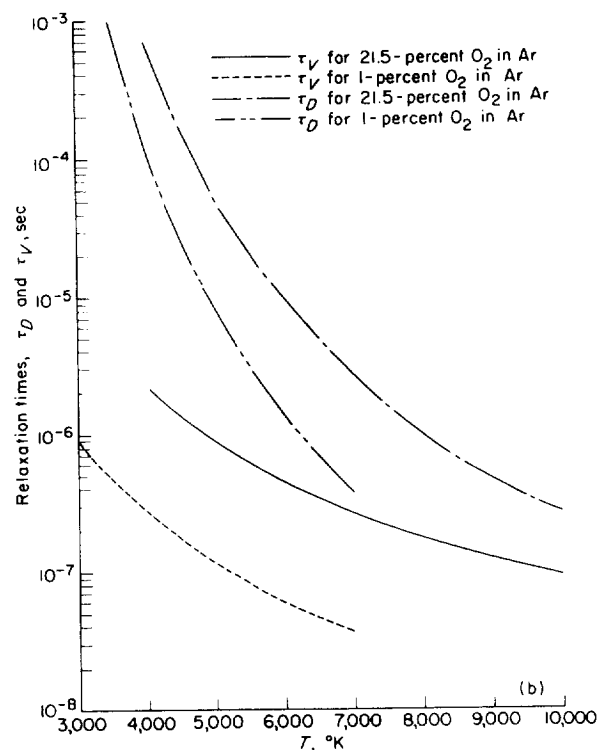
(a) Half times appropriate for this report: $p_1 = 0.5$ mm Hg for O_2 and 4 mm Hg for 10-percent O_2 in Ar; $T_1 = 300^\circ$ K. τ_V based on data of reference 13; τ_D based on data of this report.

FIGURE 11. Laboratory relaxation half times as a function of temperature.

should not have affected the k_d values reported here.

Figure 11(b) shows the laboratory vibration and dissociation relaxation times appropriate to the work reported in reference 13. A time resolution of 0.1 microsecond corresponding to the reported slit width of $\frac{1}{2}$ millimeter was used. On the basis of the curves in figure 11(b), coupling should not have affected their records for temperatures greater than about $5,000^\circ$ K for the 1-percent mixture and for temperatures greater than about $10,000^\circ$ K for the 21.5-percent mixture. Thus the effect of coupling may have been observable on some of their 21.5-percent records but not on their 1-percent records.

The laboratory vibrational relaxation times τ_V used in the preparation of figure 11 were obtained from the measured relaxation times reported in reference 13. The laboratory dissociation relaxation times τ_D in figure 11(a) were based on equations (13), (14), and (15) and in figure 11(b) the



(b) Half times appropriate for reference 13: $p_1 = 0.93$ mm Hg for 21.5-percent O_2 in Ar and 20 mm Hg for 1-percent O_2 in Ar; $T_1 = 294^\circ$ K. τ_V and τ_D based on data of reference 13.

FIGURE 11. -Concluded.

τ_D values were based on the measured rates reported in reference 13. In order to make the calculated dissociation relaxation times as short as possible, the initial values for the temperature and density ratio behind the shock front were assumed to be maintained throughout the process. This is a conservative assumption, since the actual dissociation times were longer. In the case of the relaxation times in figure 11(a) the values of p_1 and T_1 were typical of the values used for most of the tests. The calculated vibrational relaxation times shown in figure 11(a) were verified by measured values on the dissociation records when the times were long enough to be observed.

The near equality of the effective dissociation energies for oxygen and for the oxygen-in-argon mixture when all the data were used takes on added significance when compared with the results reported in reference 27 on the dissociation rate of bromine. The dissociation energy for the

bromine molecule is 45.5 kcal/mole and the D_{eff} values calculated from straight-line plots through the data reported in reference 27 are as follows:

Br ₂	30.5 kcal/mole
Br ₂ in Ar	32.2 kcal/mole

This table shows that in bromine as well as in oxygen the values of D_{eff} are much smaller than the values of D_0 .

The traces in figure 9 illustrate the variation of the experimental k_d values with $1/T$ during the various runs. The results of the alternate method for analyzing the data, the isothermal line method, are also shown in this figure. The least-square lines from figure 7 are duplicated in figure 9 in order to provide a convenient comparison reference.

The isothermal-line results and the least-squares lines follow the same general trends as the traces. In this connection it is satisfying to note that for the isothermal line method each k_d value represents an average over many tests, that for the traces each k_d value depends on local conditions behind the shock front for a particular test, and that for the least square lines the k_d values are derived from the initial portions of the traces. The agreement between these widely differing methods of analysis indicates that the rates measured at a distance far from the shock front are essentially the same as those measured near the shock front and that the results of averaging many traces are essentially the same as the results from a single trace. Thus the omission of any corrections for effects on the flow caused by the use of a small-diameter shock tube at low pressure is shown to be justified.

The recombination rate constant k_r is assumed to be related to the dissociation-rate constant k_d by the relation (eq. (9))

$$K_c = \frac{k_d}{k_r}$$

where K_c is the equilibrium constant for the dissociation reaction. Since K_c is well-known from thermodynamic calculations, k_r can be calculated from measured values of k_d on the basis of this assumption. The plot of the k_r values against T is an interesting way to compare experimentally measured values of k_d . The dissociation-rate constant k_d is generally believed to have the form

$k_d = f_1(T) \exp\left(\frac{-D_0}{RT}\right)$ and K_c is known to have the form $K_c = f_2(T) \exp\left(\frac{-D_0}{RT}\right)$. Thus $k_r = k_d/K_c$ has the form $k_r = \frac{f_1(T)}{f_2(T)}$. In other words, the strong temperature dependence of k_d due to the presence of the factor $\exp\left(\frac{-D_0}{RT}\right)$ is cancelled out so that attention can be concentrated on the remaining temperature dependence.

Figure 10 compares the k_r values derived from the k_d values shown in figure 7 and includes some measured values of k_r at room temperature taken from the literature. Some curves of k_r at high temperature for bromine, bromine in argon, and iodine in argon are also included. No corrections for collision efficiency were applied in any of the transformations. Since the efficiencies of the various atoms and molecules are not well established, it seemed best to compare the data in the original form.

All of the data in figure 10 indicate that k_r decreases with temperature. This result agrees with the result of a theoretical treatment originally due to Wigner. (See refs. 30 to 32.) The equation used for plotting Wigner's results as they apply to oxygen dissociation was taken from reference 3. One other curve in figure 10 was not calculated directly from experimental values of k_d . It represents an estimated dependence of k_r on T and was taken from reference 23. This estimated curve appears to be a reasonable compromise between the various experimental results. However, more experimental data are needed. This is especially true in the temperature region from room temperature to 4,000° K and from 7,000° K upward, in which very few measurements of k_r or k_d have been reported.

CONCLUSIONS

From the experimental data the following conclusions can be drawn.

1. The dissociation rate constant k_d for molecular oxygen has been measured in pure oxygen over the temperature range 4,000° to 9,000° K. The values obtained agree reasonably well with the experimental values found in the literature. The highest previously reported results in the literature were at 7,000° K.

2. The dissociation rate constant k_d of molecular oxygen has been measured in a mixture of 10-percent oxygen in argon over the temperature range 5,000° to 10,000° K. The highest previously reported experimental values in the literature were at 7,500° K. The k_d values agree with those obtained in pure oxygen when a correction is applied for the low efficiency factor of argon atoms relative to oxygen molecules in producing molecular oxygen dissociation.

3. The measured values of k_d in pure oxygen are about five times larger than those for the mixture. These values correspond to an efficiency factor of one-ninth for an argon atom as compared with an oxygen molecule.

4. The temperature dependence derived by fitting straight lines to the two types of measured

data is very nearly the same for both, but this temperature dependence is considerably weaker than those given in the literature at somewhat lower temperatures. By fitting a straight line to the oxygen-in-argon data over the low-temperature range, agreement is obtained with the literature data. Apparently, some mechanism caused the temperature dependence of k_d in the oxygen-in-argon mixture to decrease at high temperature. The parallel effect in pure oxygen was not evident from the observed values of k_d , but the agreement of the temperature dependence between the two sets of data points to the possibility of its presence.

LANGLEY RESEARCH CENTER,
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION,
LANGLEY FIELD, VA., March 28, 1961.

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